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# THE VAPOR PHASE AUTOXIDATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE AND 50-PERCENT UNSYMMETRICAL DIMETHYLHYDRAZINE-50-PERCENT HYDRAZINE MIXTURES

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The autoxidations of unsymmetrical dimethylhydrazine (UDMH) and a mixture of 50-percent UDMH and 50-percent hydrazine (50-50 blend) have been studied at pressures of several Torr in 44-cm reaction vessels and several ppm in a long path cell.<br><br>With initial UDMH pressures of several Torr, autoxidation proceeded too slowly to be differentiated from natural decay processes. When the initial UDMH pressure was lowered to a few ppm, the addition of oxygen caused approximately |   |   |

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20. ABSTRACT (CONCLUDED)

first order decay with a half life of about 84 hours. The main oxidation product under these conditions was formaldehyde dimethylhydrazone.

The 50-50 blend did not behave as two independent systems; instead, there were substantial positive synergistic effects observed. At concentrations of a few Torr of each component, the addition of oxygen resulted in a 10- to 20-fold increase in decay rate over that shown by UDMH or hydrazine by itself. At ppm concentration levels, the situation was similar for UDMH where a four-fold oxidation rate increase was observed when compared with a similar experiment with no hydrazine present. However, hydrazine oxidation in the 50-50 blend was somewhat slower than it was in a similar experiment with only hydrazine present.

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## PREFACE

This report documents research performed during the period January 1979 through October 1979 under Program Element 62601F, Project 1906, Subtask 2013. This research was carried out at the HQ AFESC Engineering and Services Laboratory at Tyndall Air Force Base, Florida. The author and principal investigator is Daniel A. Stone, PhD, research chemist.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

  
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## SECTION I

### INTRODUCTION

Unsymmetrical dimethylhydrazine (UDMH) is an important member of the hydrazine family of fuels. In terms of annual use, UDMH is one of the leading rocket fuels. Its low freezing point, thermal stability, and good materials compatibility make it a fuel of choice for long term storage applications.

Though several studies of UDMH air oxidation have been published in the past (References 1, 2, and 3), the present study was undertaken to extend these earlier studies to a wider range of reaction conditions. Further work on low level UDMH atmospheric degradation chemistry is being conducted under the sponsorship of the HQ AFESC Environmental Sciences Branch (Reference 4).

Though hydrazine is a more energetic fuel than UDMH, its physical properties limit its usefulness. Many mixtures of hydrazine and various materials have been formulated, but the 50-percent hydrazine - 50-percent UDMH mixture has proven most useful. This mixture is used as the fuel for the Titan II system and in other space propulsion systems.

In order to evaluate safety requirements and related environmental concerns, it is necessary that the atmospheric oxidation of UDMH and the 50-50 blend be characterized in terms of the kinetics and products of these processes.



## SECTION II

### MATERIALS

In all the experiments described in this report, the hydrazines were used as received from Rocky Mountain Arsenal (fuel grade, 98+ percent purity). The nitrogen (99.998 percent) gas, oxygen (99.99 percent) gas, and helium (99.999 percent) gas were from Air Products and Chemicals, Inc.

The 50-percent hydrazine (50-percent UDMH blend) was synthesized for each particular experimental run by expanding equal pressures of hydrazine and UDMH vapor from liquid storage bulbs into the reaction vessel using standard vacuum line techniques. For experiments carried out in the long path cell, the blend was made up of 12.72 ml of UDMH and 10.00 ml of hydrazine.

## SECTION III

### UDMH OXIDATION IN A 300-ML FLASK

#### EXPERIMENTAL

In order to compare oxidation rates and products in this current work with those of earlier studies on the oxidation of hydrazine (Reference 5) and monomethylhydrazine (Reference 6), a series of oxidations were carried out in a 300-ml Pyrex® flask equipped with a Fisher-Porter Teflon® vacuum valve and a silicon rubber septum.

Reaction mixtures were prepared as follows. The bulb was evacuated to less than 5 millitorr (as measured with a Hastings Model VH-3 thermocouple gauge) on a liquid nitrogen trapped vacuum system. The desired partial pressures of tank helium and oxygen were admitted as measured with a Wallace and Tiernan Model FA-160230 absolute pressure gauge. Finally, a Unimetrics Model 5050R syringe was used to inject the desired volume of UDMH. Mixing and vaporization were accomplished by shaking the flask which contained a few Teflon® chips.

Gas samples were analyzed on a Perkin Elmer Model 900 gas chromatograph equipped with a 6-foot by 1/4-inch stainless steel molecular sieve 5-A column (45/60 mesh) and a thermal conductivity detector. Operating conditions were: carrier gas flow 60 cc/min (helium), detector current 175 mA, injection port temperature 100°C, and detector temperature 100°C. The recorder was a Varian Model A-25 operated at 1.0 mV full scale and 0.25 in/min.

Gas sampling was accomplished with a Precision Sampling, Series A-2, 1.0-ml Pressure-Lok gas syringe, with 1.0 ml samples used throughout. For the instrument response traces and calibration curves used in this study, refer to Figures 1 and 2 of Reference 6.

#### RESULTS

First the stability of UDMH vapor in pure helium was evaluated. This was done by injecting 43  $\mu$ l of UDMH into the bulb (34.9 Torr at 25°C and monitoring nitrogen or methane production with time for 24 hours. There was no sign of either material at the 24-hour point. This is only an indirect check on UDMH stability, however, since it may degrade to products not detected by the experimental apparatus. It does show that the UDMH plus helium system is stable with respect to nitrogen or methane production.

Next an experiment was run with a 43  $\mu$ l injection of UDMH into the bulb which contained 150 Torr of oxygen and 575 Torr of helium. At the end of 71 hours there was no measurable change in oxygen concentration, and the small amount of nitrogen present at the beginning of the run remained constant. There was also no sign of any methane production. Mass spectral analysis of this sample after 71 hours showed the presence of some formaldehyde dimethylhydrazone (FDH), with traces of dimethylamine (DMA), formaldehyde monomethylhydrazone (FMH), and trimethylamine (TMA). This indicates that some oxidation had taken place but not enough to register in the relatively insensitive thermal conductivity analysis.

Finally, a run was made with a 43  $\mu$ l injection of UDMH into the bulb which contained 725 Torr of  $O_2$ . Over the course of 24 hours there was no measurable decrease in oxygen concentration or increase in nitrogen concentration. There was also no sign of any methane production. Mass spectral analysis showed an increase in FDH with traces of FMH, DMA, TMA, methanol, and N-nitrosodimethylamine present.

These results were somewhat unexpected in terms of the work on hydrazine (HZ) and monomethylhydrazine (MMH) conducted previously (Reference 5 and 6) and gave the first indication that UDMH is much more stable than either HZ or MMH with respect to thermal oxidation.

## SECTION IV

### UDMH OXIDATION IN 44-CM PATH LENGTH CELLS

#### EXPERIMENTAL

Two reaction cells were used in this study to determine the effects of surface-to-volume ratio on UDMH autoxidation. One cell had a volume of 0.14 l and a surface-to-volume ratio of  $2.0 \text{ cm}^{-1}$ , while the second had a volume of 12 l and a surface-to-volume ratio of  $0.21 \text{ cm}^{-1}$ . The infrared window-mounting system is described in Reference 5.

Infrared spectra were recorded at  $4 \text{ cm}^{-1}$  resolution with a Digilab Model FTS-20 Fourier transform infrared spectrophotometer. A Nerst glower source, potassium bromide beamsplitter, and mercury-cadmium-telluride detector (operated at  $77^\circ\text{K}$ ) were employed throughout this phase of the work. The sample cell placement and optical system are described in Reference 5.

Calibration spectra and actual experimental runs were conducted by attaching the cell (in place in the infrared optical path) to a vacuum system. While thus configured, the cell could be evacuated and filled with materials metered out to the desired pressures. Pressures of reactants were measured with a Texas Instruments Model 140 precision pressure gauge, and fill gases with a Wallace and Tiernan Model FA-160230 absolute pressure gauge. First, a reference spectrum of the cell filled with tank nitrogen, helium, or oxygen in the desired proportions was recorded and stored. Then spectra (64 coadded interferograms) of the reacting system were recorded with time and ratioed against this reference to produce absorbance spectra.

The analytical band used for UDMH calibration was the  $\text{NH}_2$  rocking band Q branch at  $908 \text{ cm}^{-1}$  (Reference 7). This band is shown in Figure 1. The calibration curve showed the same non-Beer's law behavior in the 0-5 Torr pressure range as hydrazine or monomethylhydrazine. The points were fit with a second order polynomial as shown in Figure 2.

#### RESULTS

First the stability of UDMH in pure nitrogen was checked in the 44-cm by 2-cm reaction cell (volume = 140 ml). With an initial charge of around 5 Torr of UDMH in 755 Torr of nitrogen, the natural decay half life was approximately 175 hours. When the same system was used to prepare samples of UDMH in 20 percent oxygen and 80 percent oxygen atmospheres, the decay rate was the same as with no oxygen present, within experimental error. This result was in agreement with the 300-ml bulb findings that UDMH is very stable toward air oxidation.

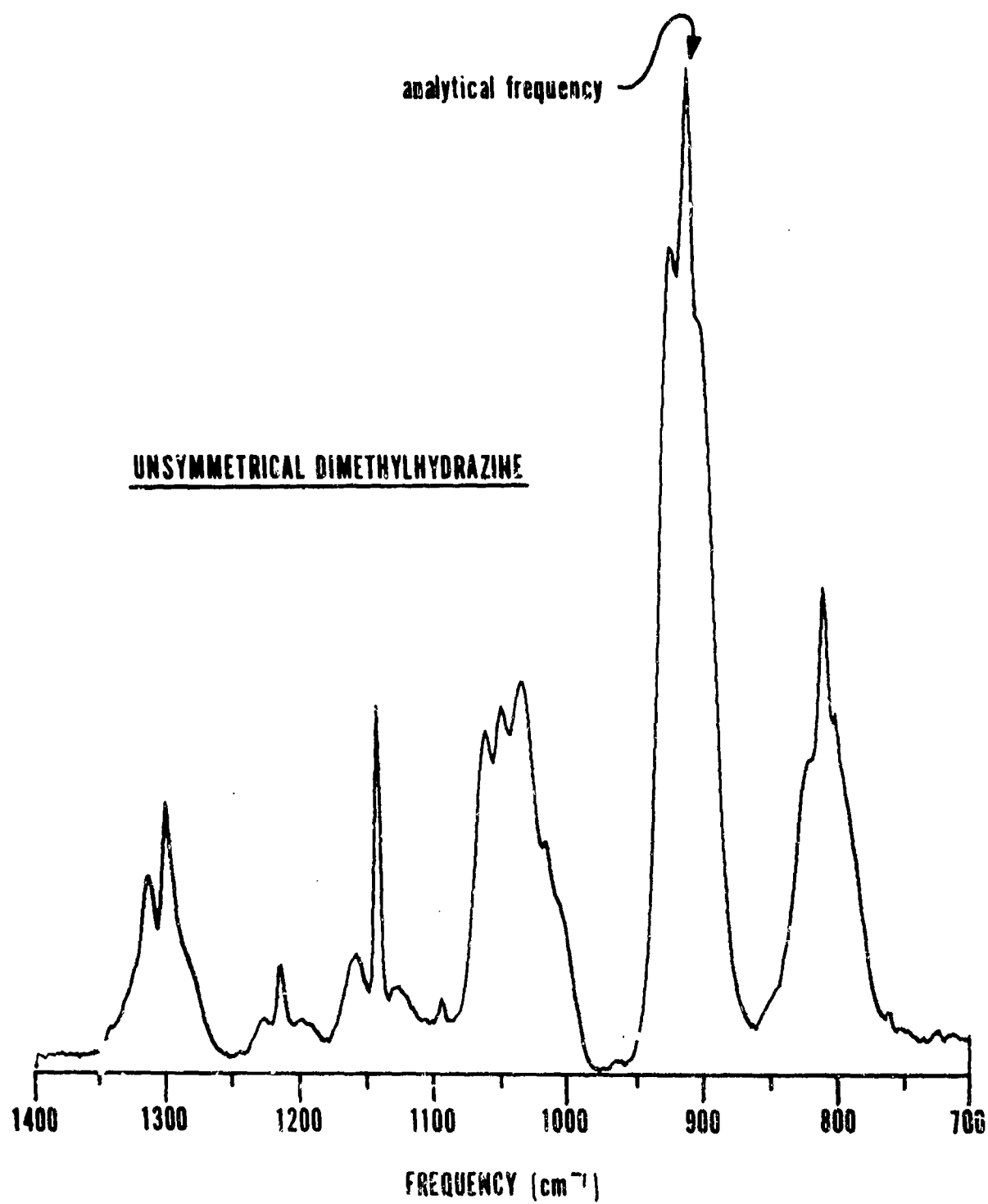


Figure 1. UDMH Infrared Spectrum ( $1\text{-cm}^{-1}$  Resolution)

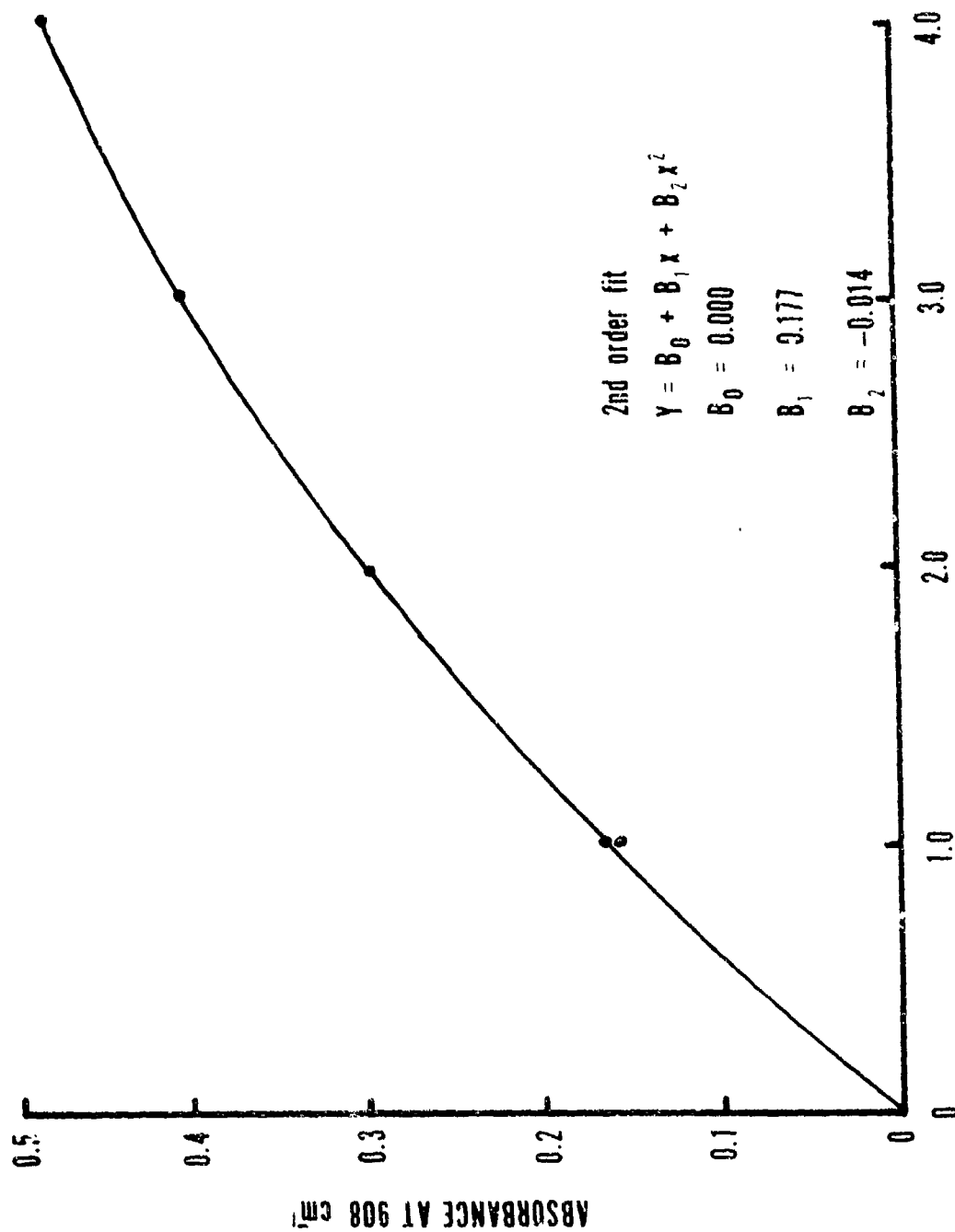


Figure 2. UDMH Absorbance Calibration Curve (44-cm X 2-cm Cell)

In runs made with the 12-liter flask, the same result was found; that is, within experimental error there was no difference in the decay rate of the UDMH in the presence of 0-, 20-, and 80-percent oxygen. The decay rate was much slower in the 12-liter flask (~ 15 percent decayed in 300 hours) but was not affected by the addition of oxygen.

Formation of a small amount of FDH in these UDMH oxidation runs was detected by the appearance of a shoulder at  $1010\text{ cm}^{-1}$  caused by a strong FDH absorbance feature. Examination of the vapor phase reaction products at the end of a run by gas chromatograph/mass spectrometer methods showed that FDH was the main oxidation product (though only about 10 to 15 percent conversion had occurred after 150 hours) with small amounts of FMH, DMA, and TMA also visible.

## SECTION V

### UDMH OXIDATION IN THE 55-LITER LONG PATH CELL

#### EXPERIMENTAL

The long path reaction cell consisted of a 0.152-meter by 3.05-meter section of Pyrex® pipe containing a three-mirror White-type (Reference 8) optical system. The base path was 2.75 meters, and the cell was operated at 68 to 74 passes to give a total path length of about 200 meters. Path length was adjusted with the aid of a helium-neon laser then experimentally verified using the methane  $1304\text{ cm}^{-1}$  Q branch transition (see Reference 6 for details of the optical system and calibration procedure). The White-cell optics were coupled to a Digilab Model FTS-20 Fourier transform infrared spectrophotometer. Spectra were recorded at  $1.0\text{ cm}^{-1}$  resolution, using 64 co-added scans and triangular apodization.

The extinction coefficient of the Q branch of UDMH at  $908\text{ cm}^{-1}$  was determined in the following manner. A Pyrex® bulb of known volume fitted with Teflon® valves on both ends was filled with UDMH to a few Torr as measured with a Texas Instrument Model 145 precision pressure gauge, then with helium to 760 Torr. This bulb was then connected to the gas distribution manifold on the long path cell and flushed into the cell, thereby being diluted to the correct concentration and turbulently mixed as pressure was raised to 760 Torr in the cell. A spectrum was recorded after allowing the sample to stabilize for 60 minutes and ratioed against a reference spectrum of the cell containing only helium. The resulting spectrum was plotted in absorbance. Using a number of different concentrations, the absorbance at  $908\text{ cm}^{-1}$  was plotted versus the product of the concentration in ppm times the path length in cm. The slope of the resulting line multiplied by  $\log_e(10)$  is the extinction coefficient. This plot is shown in Figure 3.

A typical oxidation run was conducted by filling the double ended sample bulb with a known concentration of UDMH in helium, then flushing the contents into the long path cell with fill gas. UDMH concentration with time was then monitored with the FT-IR system. One run was conducted with pure helium fill gas to check for UDMH stability in the system. Oxidation runs were conducted at 100 percent oxygen concentration to facilitate more rapid reaction rate. Oxidation was still slow enough to be neglected during the first hour while the UDMH concentration stabilized in the cell, thus ensuring an accurate starting concentration.



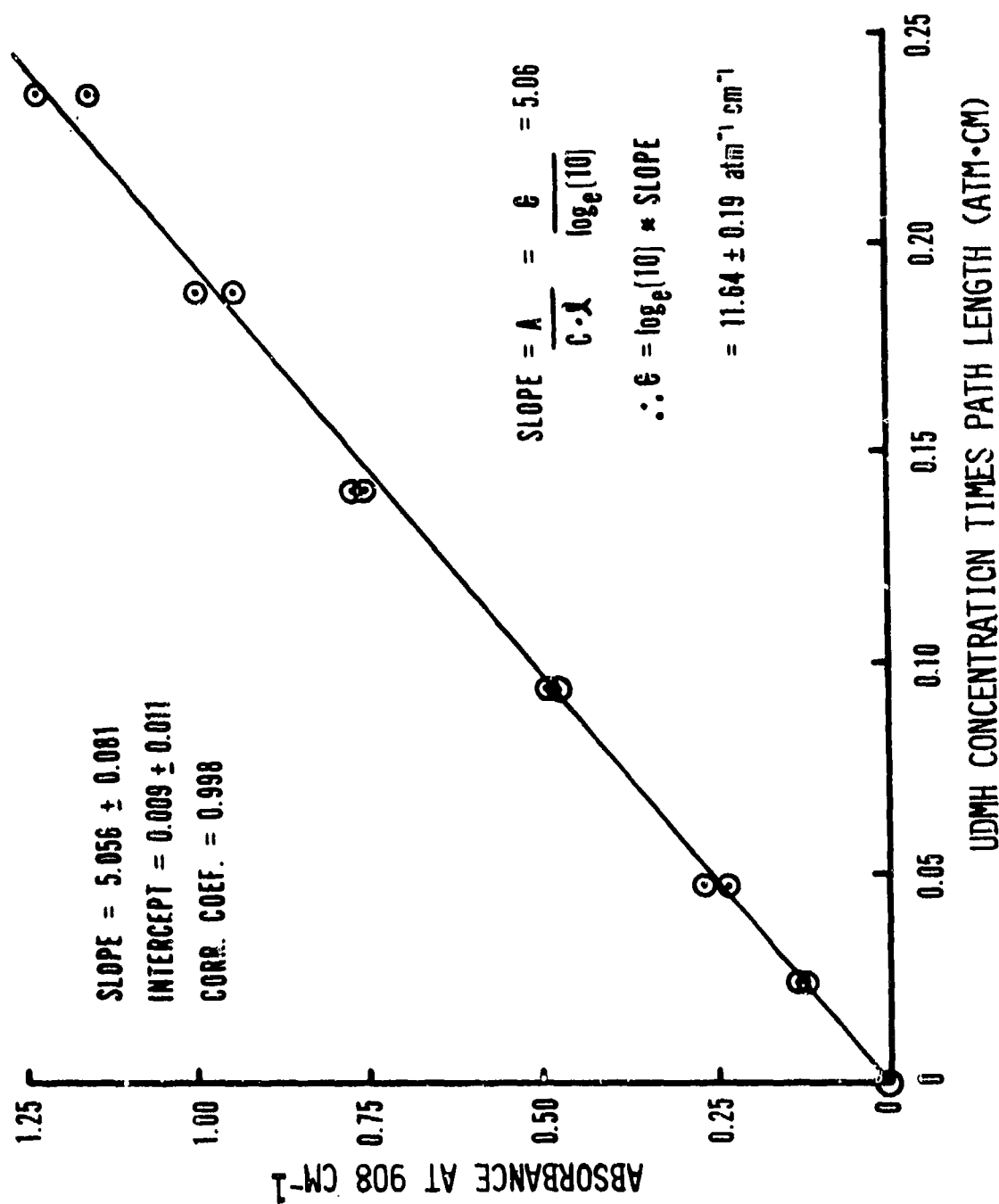


Figure 3. UDMH Absorbance at 908 cm<sup>-1</sup> Plotted versus the Concentration Times Path Length Product

## RESULTS

Unlike the high concentration oxidation experiments discussed in Section IV, those conducted in the long path cell showed an expected large difference in behavior in the presence and absence of oxygen. With no oxygen present there was a gradual decrease in UDMH concentration with time due to natural decay processes. This resulted in the loss of about 10 percent of the UDMH every 75 hours. In the presence of 100 percent oxygen (760 Torr), the UDMH followed approximately pseudo first order kinetics with a rate constant of  $8.3 \times 10^{-3} \text{ hr}^{-1}$ . This gives a half life of 83.5 hrs. The data are plotted in Figure 4.

During the course of a typical oxidation run, the spectral features of formaldehyde dimethylhydrazone (FDH) become more and more prominent. FDH is identified as the only infrared detectable product in the long path UDMH oxidation runs. Representative spectra are shown in Figure 5.

One additional set of experiments was performed in the long path cell to investigate possible photochemical influence in the UDMH autoxidation process. The long path cell is surrounded by a combination of twenty, 4-foot fluorescent black and sun lamps. With all lamps on, the  $\text{NO}_2$  photolysis constant is  $0.4 \text{ min}^{-1}$ . However, with the cell cooling system on and all the lamps on, the equilibrium operating temperature is about  $35^\circ\text{C}$ . Thus, further experimental work will be needed to differentiate between photolytic and thermal effects. Nonetheless, there was a rather pronounced difference in the reaction under photolysis conditions. FDH was visible (at  $1010 \text{ cm}^{-1}$ ) at one hour. At four hours, about half the UDMH was gone and, in addition to FDH, a major band at  $1750 \text{ cm}^{-1}$  had appeared. At the 23-hour point (7 with all lamps on), only FDH and the  $1750 \text{ cm}^{-1}$  bands were present. Then the FDH began to oxidize and by 31 hours (15 with lamps on) there was only the  $1750 \text{ cm}^{-1}$  band and small amounts of formic acid, methanol, and HCN. There was also some  $\text{N}_2\text{O}$  and CO produced. The reaction was repeated with no oxygen present. At 31 hours (15 with all lamps on) there was 35- to 45-percent conversion to FDH but only a very small band between 1700 and  $1800 \text{ cm}^{-1}$ .

## CONCLUSIONS (UDMH OXIDATION)

UDMH autoxidation proceeds about 10 times more slowly than MMH or hydrazine autoxidation under the same conditions. There appear to be different mechanisms of degradation/oxidation which operate at higher concentrations (2 to 10 Torr) and lower concentrations (2 to 10 ppm). In the higher concentration environment, degradation by absorption or other transformation processes competes equally well with oxidation losses. In the low concentration studies, oxidation was clearly the dominant loss mechanism.

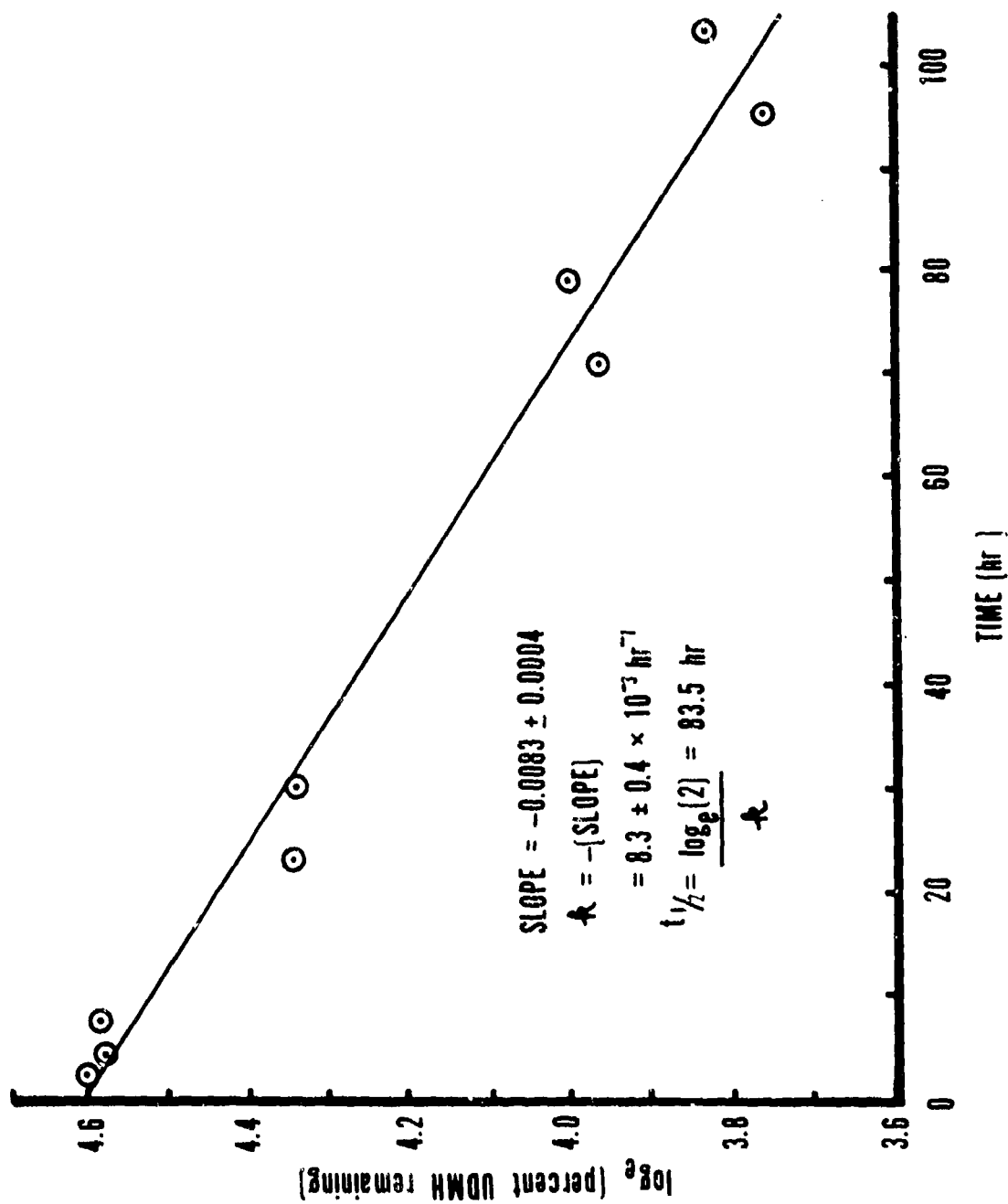


Figure 4. Plot of  $\log_e$  UDMH Concentration Versus Time Showing Pseudo First Order Decay

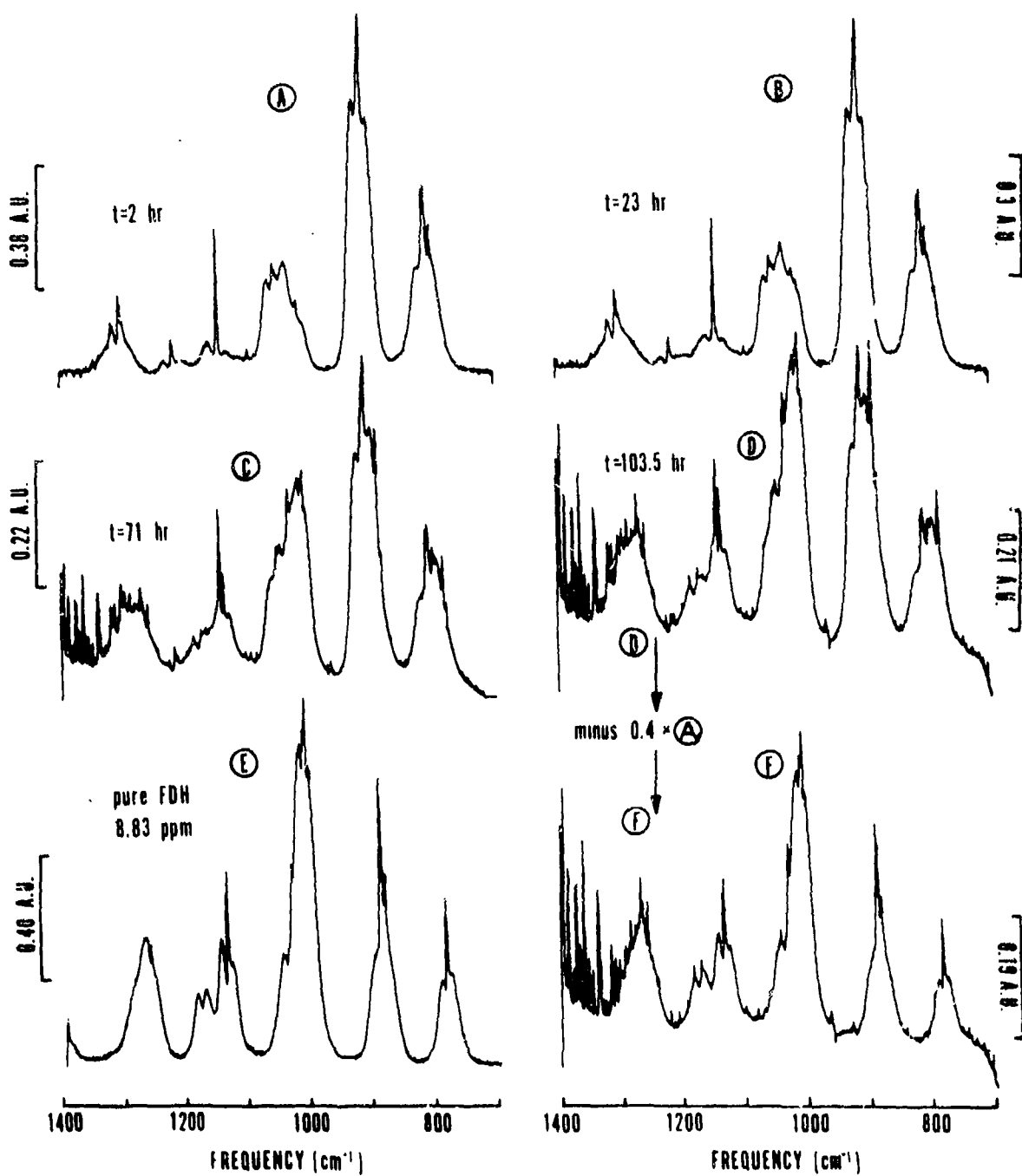


Figure 5. Infrared Spectra Recorded During A Typical UDMH Oxidation Run

The long path study lends support to the overall stoichiometry proposed by earlier workers (References 1 and 2)  $3(\text{CH}_3)_2\text{NNH}_2 + 2\text{O}_2 \longrightarrow 2(\text{CH}_3)_2\text{NNCH}_2 + 4\text{H}_2\text{O} + \text{N}_2$ . However, the studies at higher pressures, as discussed in Sections III and IV, indicate that reaction vessel size and reactant concentrations play an important role in degradation processes. This reasoning appears to be the only explanation for the differences in results between the present study and those of earlier workers (Reference 1 and 2). Using 10-cm gas cells, these workers found half lives averaging from 10 to 30 hours for different conditions and noted significant production of ammonia. Further work on the effects of different materials on UDMH degradation and oxidation will be necessary to clarify this situation.

The photolysis experiments suggest that temperature effects may be of major importance in UDMH autoxidation. Photochemical effects seem unlikely because neither UDMH or FDH absorb to any appreciable extent in the actinic UV region ( $\lambda = 290 - 400 \text{ nm}$ ) as shown in Figure 6. Further experimental work to determine the Arrhenius parameters associated with UDMH autoxidation would be very valuable.

A series of additional experiments were conducted to determine the effects of water vapor (i.e., relative humidity) on the UDMH oxidation rate. Known amounts of water vapor were added to the oxidation runs to give about 50-percent relative humidity. In both the 12-liter flask and the long path cell the reaction rate increased by about 25 percent.

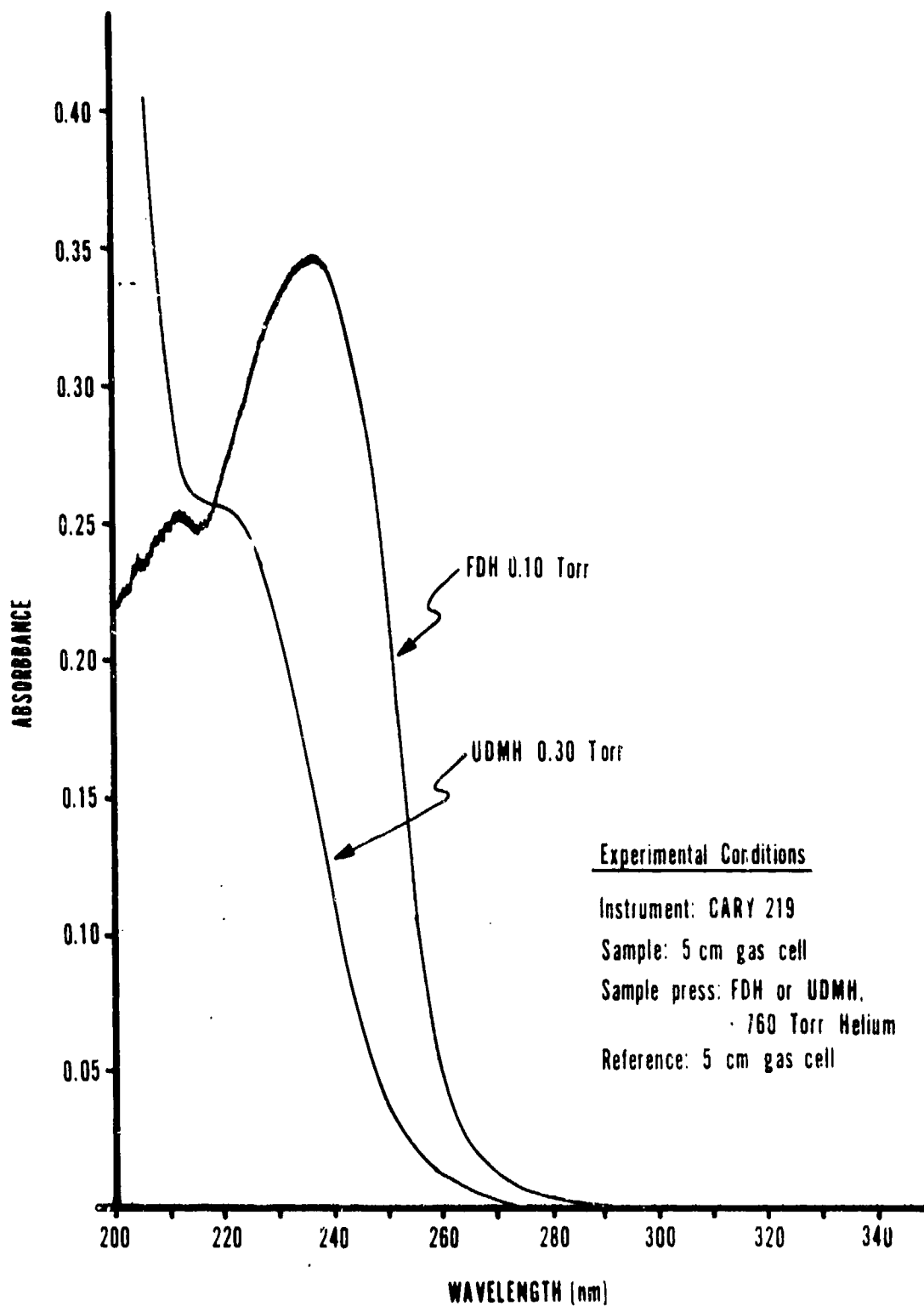


Figure 6. Ultraviolet Spectrum of UDMH and FDH

## SECTION VI

### 50-50 BLEND OXIDATION IN 44-CM PATH LENGTH CELLS

#### EXPERIMENTAL\*

The reaction cells and instrumental set up for this study are described in Section IV of this report. Samples were made up by expanding equal quantities of hydrazine and UDMH into the desired sample cell, again as described in Section IV.

Concentration values were determined by using previously recorded calibration curves for hydrazine (Reference 5) and UDMH (this report, Section IV). Hydrazine was monitored at  $958\text{ cm}^{-1}$  and UDMH at  $908\text{ cm}^{-1}$ , thus minimizing peak interference between the two species. In Figure 7 these peaks are shown in a spectrum of the 50-50 blend, along with the blend component spectra.

#### RESULTS

In the 44-cm x 2-cm cell, the components of the 50-50 blend decayed in pure helium in a manner similar to earlier individual experiments. Hydrazine half life under these conditions was around 6 hours. UDMH was, as expected, more stable with a half life greater than 50 hours, as shown in Figure 8.

The decay of the 50-50 blend in an 80-percent helium - 20-percent oxygen atmosphere was, however, much faster than the decays of the individual components in earlier studies. Whereas hydrazine by itself had a half life of around 3 hours under these conditions; as a component of the 50-50 blend, its half life decreased to around 15 minutes. Similarly with UDMH, by itself, its half life was around 150 hours, but in combination with hydrazine this was reduced dramatically to around 8 hours (see Figure 8).

In the 12-liter flask both components of the blend were very stable under oxygen-free conditions. In an atmosphere of 90 percent oxygen and 10-percent helium, both components again decayed quite rapidly. Under these conditions, hydrazine had a half life of about 40 minutes and UDMH had a half life of around 6 hours. UDMH decay appeared to exhibit a definite slowing trend as the initial hydrazine became nearly depleted, as seen in Figure 9.

\* Note: Under actual field conditions, where a spill of the 50-50 blend had occurred, the vapor composition would be given by Raoult's law. This would mean approximately 13-percent hydrazine and 87-percent UDMH as the initial composition. As evaporation continued, the vapor would become richer in hydrazine and would eventually be mostly hydrazine. In order to determine the

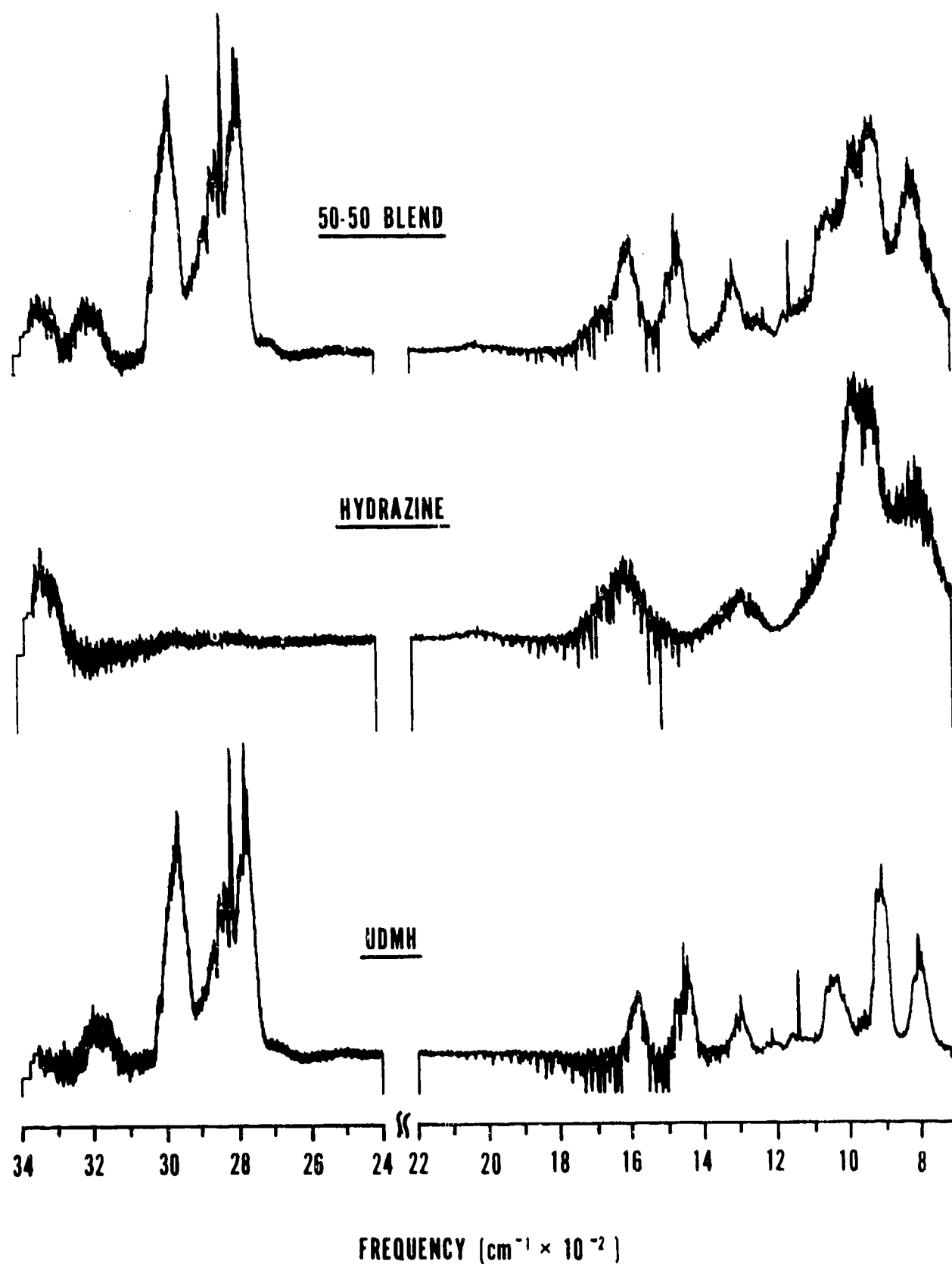


Figure 7. Infrared Spectra of Hydrazine, UDMH, and a 50-50 (weight/weight) Mixture of the Two



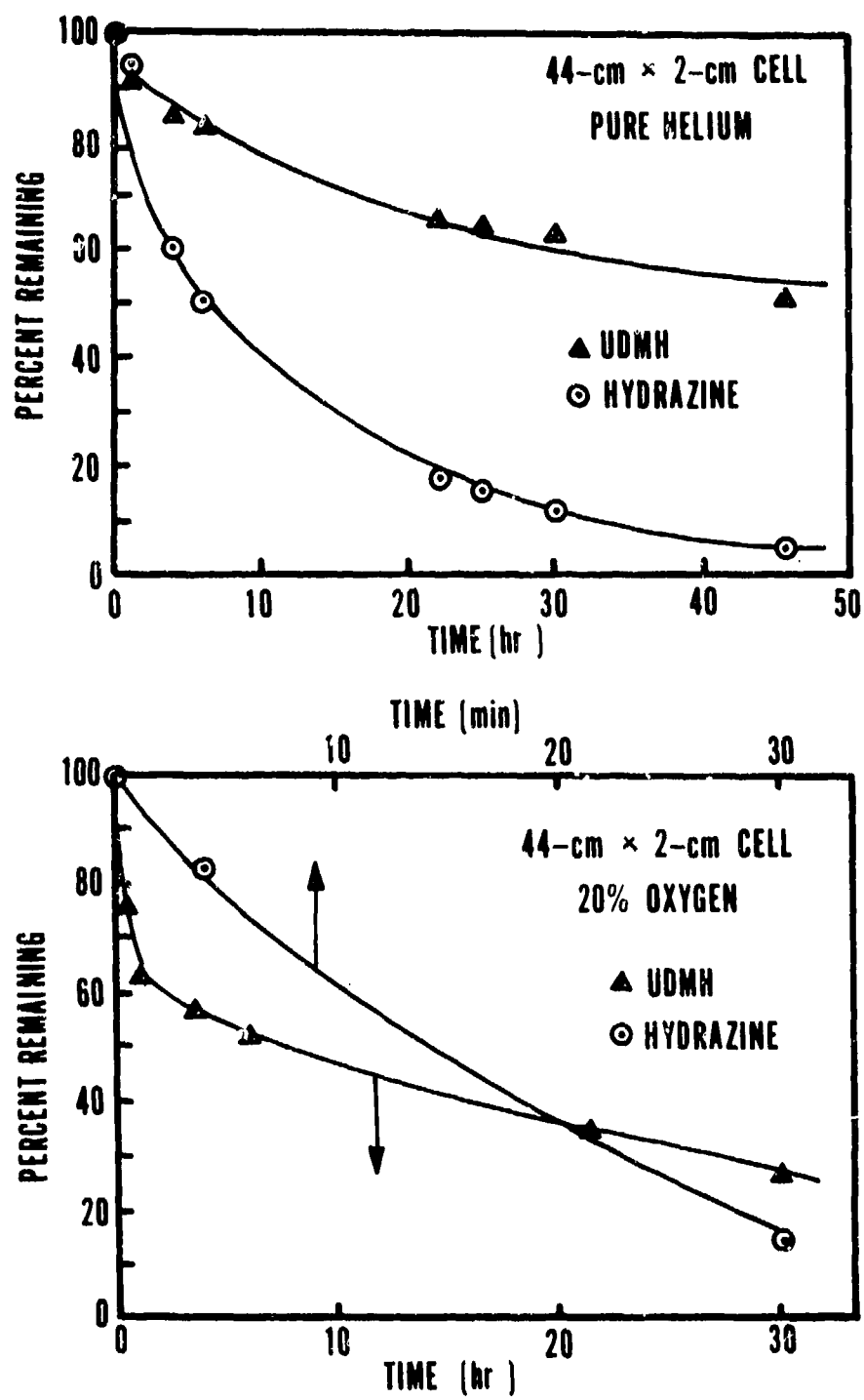


Figure 8. Plots of Hydrazine and UDMH Decay in the 44-cm X 2-cm Reaction Cell

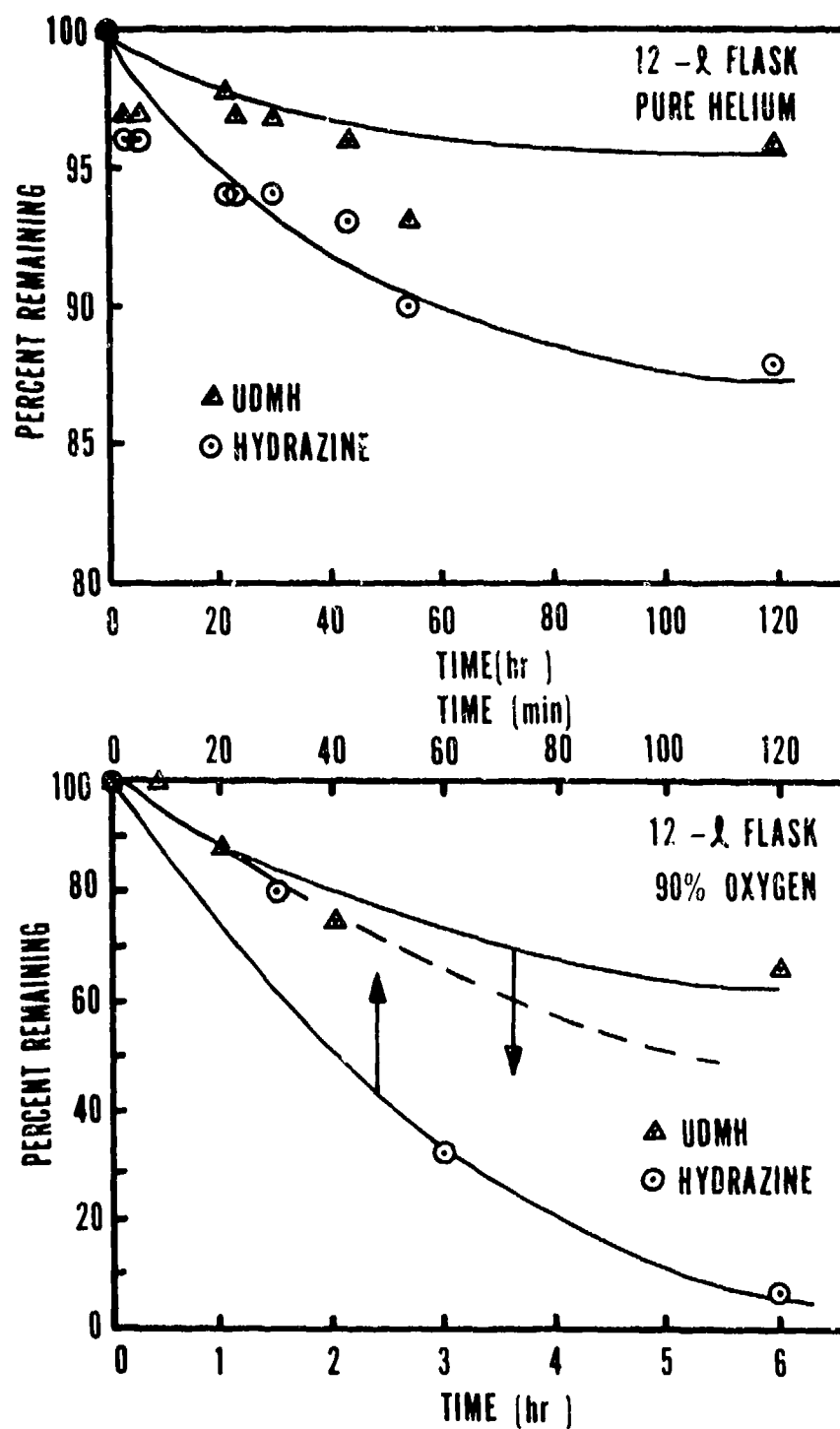


Figure 9. Plots of Hydrazine and UDMH Decay in the 12-Liter Flask

general features of the 50-50 blend autoxidation, it was decided to choose an arbitrary concentration of each component. This choice was also influenced by the relative extinction coefficients of hydrazine and UDMH. Thus, it was decided to have a vapor concentration which was 50-percent hydrazine and 50-percent UDMH.

## SECTION VII

### 50-50 BLEND OXIDATION IN THE LONG PATH CELL

#### EXPERIMENTAL

The long path cell was used for this portion of the study. The experiments were carried out as described in Section V of this report except for sample introduction. Due to previous problems in transferring gas phase samples of hydrazine to the long path cell in a quantitative fashion, it was decided to inject liquid samples of the 50-50 blend and vaporize them, then flush the vapors into the cell. This required making up a sample of liquid 50-50 blend, which was done by mixing 12.72 ml of UDMH with 10 ml of hydrazine. This gave a solution which was 50 percent by weight of each component.

The resulting spectra were analyzed for hydrazine at  $958\text{ cm}^{-1}$  ( $\epsilon = 2.77\text{ atm}^{-1}\text{ cm}^{-1}$ ) and for UDMH at  $908\text{ cm}^{-1}$  ( $\epsilon = 11.64\text{ atm}^{-1}\text{ cm}^{-1}$ ).

#### RESULTS

In an atmosphere of pure helium, UDMH was very stable showing very little decay over a 24-hour period. Hydrazine, on the other hand, was quite unstable, having a half life of about 15 hours.

Upon adding the 50-50 blend to a mixture of 20-percent oxygen and 80-percent helium, the situation changed considerably. The UDMH decay rate increased to give an approximate 20-hour half life, while the hydrazine half life accelerated to around 5 hours. These results are shown in Figure 10.

When compared to the separate earlier studies involving UDMH and hydrazine autoxidations under similar conditions, the present half life for UDMH is much shorter, while that for hydrazine is about twice as long.

#### CONCLUSIONS

The autoxidation of a 50-50 blend of hydrazine and UDMH proceeds to give the same infrared detectable products as the autoxidations of the individual components. That is, hydrazine produces ammonia and water and UDMH produces formaldehyde dimethylhydrazone. However, there is a rather dramatic increase in reaction rate when the two components are combined as the 50-50 blend, except for hydrazine in the long path cell where the rate was unexpectedly decreased. The resultant half lives range from a few minutes for hydrazine to a few hours for UDMH.

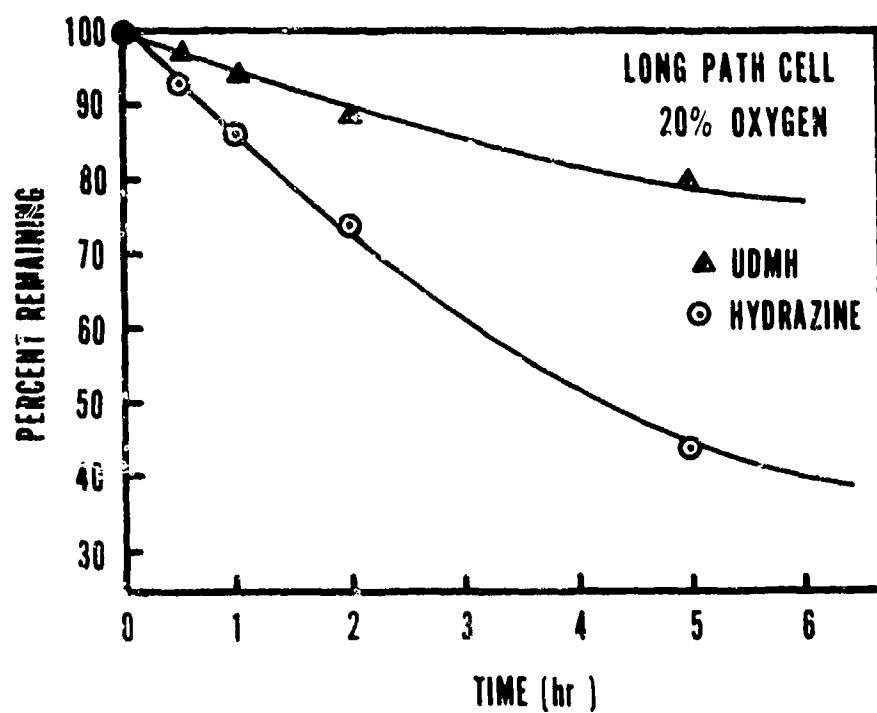
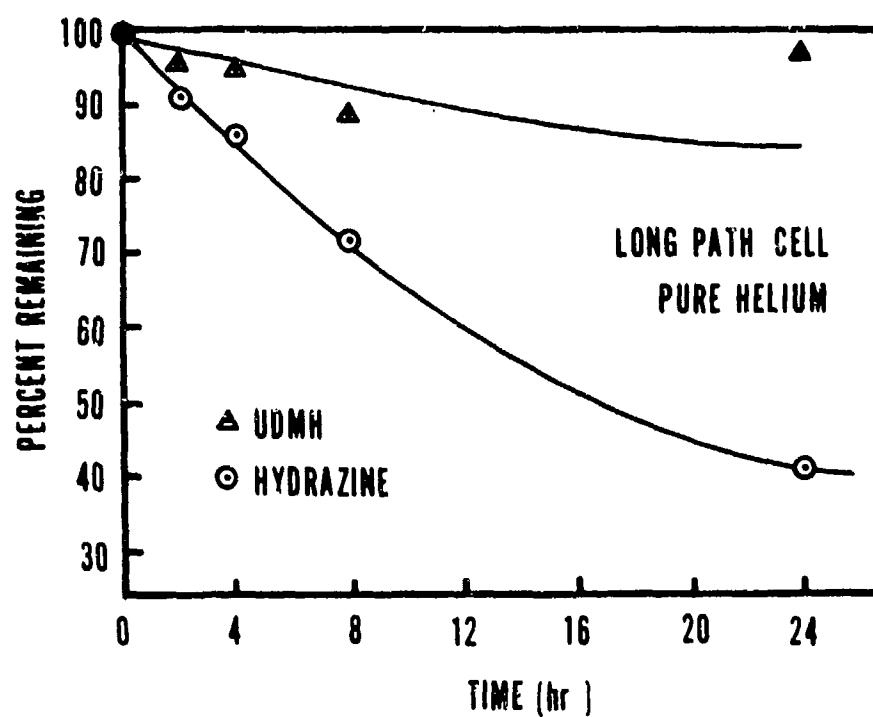


Figure 10. Plots of Hydrazine and UDMH Decay in the Long Path Cell

Earlier workers (References 1 and 9) have postulated a free radical reaction mechanism for the autoxidation of hydrazine and UDMH. If such a mechanism is correct, then the positive synergistic effect of the combination of hydrazine and UDMH on their respective autoxidation processes is possibly a reflection of newly opened radical initiation or propagation steps. Further work on the mechanisms of each component and the 50-50 blend will be necessary to clarify the details of these intermediate reaction steps.

This portion of the study has demonstrated that a spill of 50-50 blend would degrade more rapidly in air than either of its components would separately. This would lessen, to this degree, the problems posed by possible downwind exposure to the combination of these two fuels.

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